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RHEOLOGICAL BEHAVIOR OF DILUTE SUSPENSIONS OF SOLID VISCOELASTIC SPHERES IN A NEWTONIAN FLUID

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An analysis is presented of the motion of individual spheres of a viscoelastic solid suspended in a Newtonian fluid which undergoes a time-dependent homogeneous deformation. For the case of small deformation of the particles, the results of this analysis are then employed to deduce the macroscopic rheological behavior of a dilute monodisperse suspension of such particles.

For the special case of purely elastic particles, the rheological relation obtained here is found to differ from that presented in an earlier work of Fröhlick and Sack (1946), by the appearance of certain nonlinear terms in the rate of deformation tensor. Moreover, the equation presented here for elastic particles turns out to be a special case of Oldroyd's (1958) general equation, with constants which can be directly related to the suspension properties.

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1. INTRODUCTION

The problem of deducing theoretically the macroscopic rheological behavior of microscopically heterogeneous fluids has received considerable attention dating from the celebrated early work of Einstein on the

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viscosity of dilute suspensions of solid spheres in Newtonian liquids.

Due to their particular relevance to an understanding of elastic effects in emulsions as well as perhaps in solutions of deformable macromolecules, mathematical models for suspensions of deformable elastic particles have received a good deal of attention. Following the work of Fröhlich and Sack (1946) on the irrotational flow of dilute suspensions of elastic spheres, Oldroyd (1953, 1955) treated suspensions of liquid droplets exhibiting interfacial effects and he raised some interesting questions as to the appropriate generalizations of Fröhlich and Sack's equations to general flows with rotation included. More recently Giesekus (1962) has made both experimental and theoretical studies of deformable particles in certain types of shear fields, the theoretical studies dealing with simplified hydrodynamic models.

The present analysis treats suspensions of solid viscoelastic spheres, a problem considered earlier by Cerf (1951) in connection with a study of flow birefringence of polymer solutions. However, Cerf did not consider the rheology of such suspensions in great detail, and the present study was undertaken in the hope of elucidating the effect of shear-induced particle deformation and rotation on suspension behavior, when such effects as Brownian motion can be considered negligible.

After considering first here the motion of individual, isolated particles suspended in a Newtonian fluid, we shall consider the behavior of dilute suspensions.

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1.1 Motion of a single viscoelastic sphere in a homogeneous velocity-gradient field.

We wish to derive here the equations describing the simultaneous rotation and deformation of a single viscoelastic particle placed in a time-dependent flow field of an incompressible Newtonian fluid with a homogeneous, i.e., spatially uniform, velocity gradient.

We shall assume that the particle is composed of a homogeneous and isotropic, solid-like material and that, in its natural or undeformed, stress-free state, the particle is spherical in shape. Furthermore, we shall suppose that the rheological constitutive equation of the solid is known so that, once the stress history is completely specified over the surface of the particle, its instantaneous deformation can in principle be determined.

The problem consists therefore of determining the motion and deformation of the particle when it is placed in an infinite flow field whose (time-dependent) velocity distribution, the "undisturbed" flow, is prescribed far from the particle. This is a well-known type of problem which involves the simultaneous solution of the equations of motion of the fluid and of the particle, with a matching of the local stress velocity or displacement at the particle surface. Since we shall assume here the absence of interfacial effects, this matching can be imposed on all the components of the velocity vector and stress tensor.

We shall further assume that the density of the particles is identical to that of the fluid, or that buoyancy forces are otherwise negligible and, as an approximation, that inertial forces are everywhere negligible beside elastic and viscous forces. In this case, the equations governing the motion of the fluid reduce to the well-known Stokes equations:

$$\begin{aligned} \mu \nabla^2 \mathbf{v} &= \nabla p \\ \nabla \cdot \mathbf{v} &= 0 \end{aligned} \tag{1.1}$$

where $\mathbf{v} = \mathbf{v}(\mathbf{r},t)$ and $p = p(\mathbf{r},t)$ are the vector velocity field and the pressure field in the fluid and μ the fluid viscosity, with $\mathbf{r}$ and t denoting, respectively, the position vector and time. The criteria for validity of the Stokes approximation for problems of the present type have been rather throughly discussed elsewhere (e.g., by Happel and Brenner, 1965) and we shall not elaborate further here on this point.

Now, once the appropriate rheological equation for the particle is specified a second equation of motion, the analogue of (1.1), can be written down for the region occupied by the particle. Then, letting primed quantities refer to this region and matching velocity and stress at the surface of the particle $\mathcal{S}'(t)$, say, we shall have:

$$\left.\begin{aligned} \mathbf{v}(\mathbf{r},t) &= \mathbf{v}'(\mathbf{r},t) \\ \mathbf{T}(\mathbf{r},t) &= \mathbf{T}'(\mathbf{r},t) \end{aligned}\right\} \quad \text{for } \mathbf{r} \text{ on } \mathcal{S}'(t) \tag{1.2}$$

where $\mathbf{T}(\mathbf{r},t)$ is the stress tensor, a second-order tensor field. As is done here, we shall mainly employ Gibbs' dyadic notation for tensors in the following analysis, with vectors and tensors denoted by bold face lower- or upper-case letters, respectively.

One further condition on fluid velocity, far from the particle, will then suffice in principle for determination of the motion. Letting $\mathbf{r}$

denote henceforth the position vector referred to the mass center of the particle, we shall take this remaining condition to be

$$\underset{\sim}{v} + \underset{\sim}{v}^{(o)} = \underset{\sim}{\Gamma}^{(o)} \cdot \underset{\sim}{r}, \text{ for } r \to \infty \tag{1.3}$$

where $r = |\underset{\sim}{r}|$ and $\underset{\sim}{\Gamma}^{(o)}(t)$ is a velocity-gradient tensor, $\underset{\sim}{v}^{(o)}$ being the "undisturbed" flow velocity.

Having thus posed the problem, at least up to a specification of the rheological equation for the particle, we are led now to an observation which will greatly facilitate its solution. In particular, if the material of the particle is homogeneous and isotropic and if its instantaneous strain depends only on the past history of stress, it is plausible to suppose, at least for solid-like materials, that the motion of the original sphere will consist of a rigid body rotation plus a homogeneous deformation or, more precisely, that the velocity-gradient field is homogeneous inside the particle. This supposition can be justified heuristically by noting, first of all, that under a homogeneous deformation a spherical or ellipsoidal particle will be transformed at any instant into an ellipsoid; furthermore, one can deduce from classical work of Jeffrey (1922) that, for the motion of rigid solid ellipsoids in homogeneous velocity-gradient fields, the fluid stress on the surface of the ellipsoids gives rise to a homogeneous stress field inside the ellipsoid. Provided then, in the present case, that a homogeneous stress history gives rise to homogeneous strain in the particle, it remains only to show that Jeffrey's result carries over to deformable spheres or ellipsoids. Indeed this is possible and, moreover, the complete solution to the present problem can be constructed readily by a slight modification of Jeffrey's results, as we now show.

1.2 Extension of Jeffrey's result to deformable ellipsoids.

First of all, we begin by assuming that the stress inside the particle is homogeneous; as a consequence, we can express the velocity $\underset{\sim}{v}'$ in the first equation of (1.2) by

$$\underset{\sim}{v}' = \underset{\sim}{\Gamma}'\cdot\underset{\sim}{r}$$

where $\underset{\sim}{\Gamma}' = \underset{\sim}{\Gamma}'(t)$, independent of position, is the velocity-gradient tensor inside the particle. Next, decomposing $\underset{\sim}{\Gamma}'$ into a symmetric strain-rate tensor $\underset{\sim}{E}'$ and an antisymmetric "rotation" tensor $\underset{\sim}{\Omega}'$, we have

$$\underset{\sim}{\Gamma}' = \underset{\sim}{E}' + \underset{\sim}{\Omega}' \tag{1.4}$$

and the angular velocity vector of the particle is simply $-\frac{1}{2}\,\mathrm{Vec}\,\underset{\sim}{\Omega}'$.

Thus, Equation (1.2) can be replaced by

$$\underset{\sim}{v}' = (\underset{\sim}{E}'+\underset{\sim}{\Omega}')\cdot\underset{\sim}{r}, \text{ for } \underset{\sim}{r} \text{ on } \mathcal{S}'(t) \tag{1.5}$$

where $\mathcal{S}'(t)$ is now an ellipsoidal surface. It follows then that, for a given $\underset{\sim}{E}'$ and $\underset{\sim}{\Omega}'$, the fluid motion outside the particle could be determined from (1.1), (1.3) and (1.5).

In contrast to the foregoing problem statement, the problem treated by Jeffrey requires the solution of Equation (1.1) subject to the conditions

$$\begin{aligned} \underset{\sim}{v} &= \underset{\sim}{\Omega}'\cdot\underset{\sim}{r} && \text{for } \underset{\sim}{r} \text{ on } \mathcal{S}'(t) \\ \underset{\sim}{v} &\to \underset{\sim}{\Gamma}^{(o)}\cdot\underset{\sim}{r} && \text{for } r \to \infty \end{aligned} \tag{1.6}$$

where again $\mathcal{S}'(t)$ is an ellipsoidal surface and where $\underset{\sim}{\Omega}' = \underset{\sim}{\Omega}'(t)$ and

$\Gamma^{(o)} = \Gamma^{(o)}(t)$. These equations govern the motion of a rigid ellipsoid in the absence of any externally applied force, and as shown by Jeffrey the solution to this problem permits determination of Ω', i.e., of the particle rotation, once $\Gamma^{(o)}$ and any extraneous torques on the particle are specified.

Considering here the case of zero torque only, we denote Jeffrey's solution for the fluid velocity, pressure field, and particle rotation, respectively, by

$$
\begin{aligned}
v &= u\{\Gamma^{(o)};r,t\} \\
p &= q\{\Gamma^{(o)};r,t\} \qquad (1.8) \\
\text{and} \quad \Omega' &= W\{\Gamma^{(o)};r,t\}
\end{aligned}
$$

without writing any of these down more explicitely for the moment. However, because of the linearity of Equations (1.1) and due to the absence of time derivatives in the problem, it follows immediately from (1.6) that the functions

$$
\begin{aligned}
v &= u\{\Gamma^{(o)}-E';r,t\}+E'\cdot r \\
p &= q\{\Gamma^{(o)}-E';r,t\} \qquad (1.9) \\
\Omega' &= W\{\Gamma^{(o)}-E';r,t\}
\end{aligned}
$$

will satisfy (1.1), (1.3) and (1.5), provided of course that the surface $\mathcal{S}'(t)$ in (1.5) is taken to coincide instantaneously with that in (1.6), and provided further that

$$\nabla\cdot(E'\cdot r) \equiv \mathrm{tr}\,(E') \equiv \nabla\cdot v' = 0$$

where "tr" denotes the trace of a tensor. This latter condition corresponds to incompressibility of the particles and, although it does not appear to be strictly necessary to the proof at hand, we shall assume henceforth that the particles are indeed composed of an incompressible material.

It remains now only to observe that Jeffrey's results yield for the stress (tensor) field

$$\underset{\sim}{T} = \underset{\sim}{T}'\{\underset{\sim}{\Gamma}^{(o)};t\} \qquad \text{for } \underset{\sim}{r} \text{ on } \mathcal{S}'(t) \tag{1.10}$$

i.e., $\underset{\sim}{T}'$ is independent of position on the particle surface.

It follows readily then, from the equation of equilibrium of forces, that $\underset{\sim}{T}'$ represents the stress tensor at any point inside the ellipsoid, if inertial effects are negligible. Otherwise stated, the fluid stress produces a homogeneous stress inside a rigid ellipsoid, a fact emphasized earlier by Cerf (1951). On the other hand, for a deforming ellipsoid the preceding equation should be replaced by

$$\underset{\sim}{T} = \underset{\sim}{T}'\{\underset{\sim}{\Gamma}^{(o)}-\underset{\sim}{E}';t\}+2\mu\underset{\sim}{E}'(t) \qquad \text{for } \underset{\sim}{r} \text{ on } \mathcal{S}'(t) \tag{1.11}$$

which can be deduced from (1.9), as will be shown in the following section.

Hence, it follows that our initial assumption of homogeneous strain in the particle is justified provided, of course, that the homogeneous stress in (1.10) is rheologically consistent with such a deformation. Moreover, as indicated by (1.9), the solution to the present problem can be derived directly from Jeffrey's results, and we shall now exploit this rather fortunate circumstance.

1.3 Motion of a slightly deformable sphere.

In the present work we shall restrict our attention to spherical particles with sufficient rigidity to insure that their deformations are always small, although this is not strictly necessary for validity of the analysis. In particular, and exactly as is done in the classical (linear) theory of elasticity, we shall assume that second- and higher-order terms in the (components of the) strain tensor are all negligible. The necessary conditions for small strains in the present problem will be stated more precisely below.

We let now a_o denote the radius of the underformed sphere and $a_i(t)$, $i=1,2,3$, the semi-principal axes of the ellipsoid resulting from its deformation. Denoting further the finite strain tensor by $\underset{\sim}{C}'$ and the Cauchy-Green deformation tensor by $\underset{\sim}{G}'$ we shall define the latter by taking its components to be

$$G'_{ij} = \begin{cases} (a_o/a_i)^2 & \text{for } i=j \\ 0 & \text{for } i \neq j \end{cases} \tag{1.12}$$

on an orthogonal Cartesian coordinate system $x_i(i=1,2,3)$ chosen to coincide with the principal axes of deformation, while we define the former by

$$\underset{\sim}{G}' = \underset{\sim}{I} - 2\,\underset{\sim}{C}' \tag{1.13}$$

on an arbitrary system. The equation of the (ellipsoidal) surface of the particle is merely that of the ellipsoid of the tensor $\underset{\sim}{G}'$, i.e.,

$$\sum_{i=1}^{3}\left(\frac{x_i}{a_i}\right)^2 = \frac{\underset{\sim}{r}\cdot\underset{\sim}{G}'\cdot\underset{\sim}{r}}{a_o^2} = 1$$

the last equality holding of course in any coordinate frame.

By differentiating the preceding relation with respect to t and by noting that

$$\frac{d\underset{\sim}{x}}{dt} = \underset{\sim}{v}' = \underset{\sim}{\Gamma}'\cdot\underset{\sim}{x} \qquad \text{for } \underset{\sim}{x} \text{ on } \mathcal{S}'(t)$$

one has that

$$\frac{d\underset{\sim}{G}}{dt} + (\underset{\sim}{\Gamma}')^{\dagger}\cdot\underset{\sim}{G} + \underset{\sim}{G}\cdot\underset{\sim}{\Gamma}' = \underset{\sim}{0}$$

or, in terms of $\underset{\sim}{C}'$ and $\underset{\sim}{E}'$, that

$$\underset{\sim}{E}' = \frac{d\underset{\sim}{C}'}{dt} - \underset{\sim}{\Gamma}'\cdot\underset{\sim}{C}' - \underset{\sim}{C}'\cdot(\underset{\sim}{\Gamma}')^{\dagger} \tag{1.14}$$

Here, $(\underset{\sim}{\Gamma}')^{\dagger}$ denotes the transpose or dydadic conjugate of $\underset{\sim}{\Gamma}'$ which by (1.3) is

$$(\underset{\sim}{\Gamma}')^{\dagger} = \underset{\sim}{E}' - \underset{\sim}{\Omega}' \tag{1.15}$$

since $(\underset{\sim}{E}')^{\dagger} = \underset{\sim}{E}'$ and $(\underset{\sim}{\Omega}')^{\dagger} = -\underset{\sim}{\Omega}'$. Equation (1.14) will be recognized as the definition of $\underset{\sim}{E}'$ in terms of a "convected" derivative of $\underset{\sim}{C}'$.

In order to express certain of Jeffrey's results in the present notation, we recall that the components of $\underset{\sim}{C}'$ on the axes of the ellipsoid are

$$C'_{ij} = \begin{cases} \frac{1}{2}\left[1 - \left(\frac{a_o}{a_i}\right)^2\right] & \text{for } i=j \\ 0 & \text{for } i\neq j \end{cases}$$

i,j=1,2,3. Hence, for the present purposes, it suffices to consider the semi-principal axes of the ellipsoid in Jeffrey's paper to be functions of time $a_i(t)$.

However, by restricting ourselves to the case of small strains, we have that

$$\frac{a_1}{a_0} = 1 + C'_{11} + \frac{3}{2} C'^{2}_{11} + O(C'^{3}_{11}) \tag{1.16}$$

with similar equations for $i=2,3$. If then these expressions for $a_i(t)$ in terms of the $C'_{ii}(t)$ are substituted into Jeffrey's expression for the fluid stress on the surface of a rigid ellipsoid, one finds after some algebra that the components of the stress tensor in (1.10) $\tilde{T}'$ expressed on the axes of the ellipsoid are

$$\begin{aligned} T_{11}' &= \mu\{5E_{11}^{(o)}(1 + \frac{6}{7} C_{11}') + \frac{4}{7} [E_{22}^{(o)}(C_{11}'-C_{22}') \\ &\quad + E_{33}^{(o)}(C_{33}'-C_{11}')] + O(C'^2)\} + p^{(o)} \qquad (1.17) \\ T_{12}' &= 5\mu E_{12}^{(o)}(1 - \frac{3}{7} C_{33}') + O(C'^2) \end{aligned}$$

with similar expressions for T_{22}', T_{23}', etc., obtained by cyclic permutation of the indices 1, 2, 3. Here $p^{(o)} = p^{(o)}(t)$ is the undisturbed pressure field far from the ellipsoid, $E_{ij}^{(o)} = E_{ij}^{(o)}(t)$ are the components of the deformation-rate tensor for the undisturbed flow (again expressed on the axes of the ellipsoid), and $O(C'^2)$ denotes quantities which involve terms of the second order in C_{11}', C_{22}', and C_{33}'. To derive the preceding relations from those given by Jeffrey, we have made use of the fact that the condition for incompressibility of the solid sphere:

$$a_1 a_2 a_3 = a_o^3 \cancel{(\text{or}, \tilde{C}':\tilde{C}'=1)}$$

reduces for small $\tilde{C}'$ to

$$C_{11}'+C_{22}'+C_{33}'-2(C_{11}'C_{22}'+C_{11}'C_{33}'+C_{22}'C_{33}')+ O(C'^3) = 0$$

In this regard we should note that it is necessary to retain the terms of the second order in the preceding relation as well as those in (1.16) if one is to arrive at the correct expression for terms of the first order in (1.17) (by expansion of the integrals, denoted by α_o, β_o, $\gamma_o,\ldots$, in Jeffrey's paper, in terms of the C'_{ii}).

Now, Equation (1.17) can be expressed in dyadic notation by noting that on the present coordinate system ($C'_{ij}=0$, $i\neq j$) it is merely

$$\underset{\sim}{T}' = \mu\{5\underset{\sim}{E}^{(o)} + \frac{15}{7}[\underset{\sim}{E}^{(o)}\cdot\underset{\sim}{C}'+\underset{\sim}{C}'\cdot\underset{\sim}{E}^{(o)}] + \frac{4}{7}(\underset{\sim}{E}^{(o)}:\underset{\sim}{C}')\underset{\sim}{I}\} - p^{(o)}\underset{\sim}{I} + O(C'^2) \tag{1.18}$$

where

$$\underset{\sim}{E}^{(o)} = \frac{1}{2}[\underset{\sim}{\Gamma}^{(o)} + (\underset{\sim}{\Gamma}^{(o)})^{\dagger}]$$

and

$$\underset{\sim}{E}^{(o)}:\underset{\sim}{C}' = \mathrm{tr}\,(\underset{\sim}{E}^{(o)}\cdot\underset{\sim}{C}')$$

Also, $\underset{\sim}{I}$ denotes the unit tensor and $\underset{\sim}{E}^{(o)}$ is of course the deformation rate tensor for the undisturbed flow in Jeffrey's problem. Stated in the form (1.18), the above relation must be valid now on any coordinate system.

Now, since we are dealing here with isotropic materials, it is necessary to consider only the deviatoric stress tensor, or non-isotropic part of $\underset{\sim}{T}$, defined by

$$\underset{\sim}{P} = \underset{\sim}{T} + p\,\underset{\sim}{I} \tag{1.19}$$

where

$$p = -\frac{1}{3}\,\mathrm{tr}\,\underset{\sim}{T} \equiv -\frac{1}{3}\,\underset{\sim}{T}:\underset{\sim}{I}$$

is the pressure. In terms of $\underset{\sim}{P}$, (1.18) becomes then

$$\underset{\sim}{P}' = 5\mu\{\underset{\sim}{E}^{(o)} + \frac{3}{7}(\underset{\sim}{E}^{(o)}\cdot\underset{\sim}{C}'+\underset{\sim}{C}'\cdot\underset{\sim}{E}^{(o)}) - \frac{2}{7}(\underset{\sim}{E}^{(o)}:\underset{\sim}{C}')\underset{\sim}{I}\} + O(C'^2)\ldots \tag{1.20}$$

which gives the deviatoric stress inside rigid ellipsoids due to the action of fluid stresses at the surface. For incompressible Newtonian fluids these stresses are given by

$$\underset{\sim}{P} = 2\,\mu\,\underset{\sim}{E} \tag{1.21}$$

where

$$\underset{\sim}{E} = \frac{1}{2}\,[\underset{\sim}{\nabla}\,\underset{\sim}{v} + (\underset{\sim}{\nabla}\,\underset{\sim}{v})^{\dagger}]$$

is the deformation rate tensor field for the fluid ($\underset{\sim}{\nabla}\underset{\sim}{v}$ has components $\partial v_i/\partial x_j$ on an orthogonal Cartesian system x_i). It follows then from the considerations of the preceding section, in particular from the first equation of (1.9), that for deformable ellipsoids we shall have now instead of (1.20)

$$\begin{aligned}\underset{\sim}{P}'(t) \;=\; & 5\mu\{\underset{\sim}{A} + \frac{3}{7}\,(\underset{\sim}{A}\cdot\underset{\sim}{C}'+\underset{\sim}{C}'\cdot\underset{\sim}{A}) - \frac{2}{7}\,(\underset{\sim}{A}:\underset{\sim}{C}')\underset{\sim}{I}\} \\ & + 2\mu\,\underset{\sim}{E}' + O(C'^2)\ldots\end{aligned} \tag{1.22}$$

where

$$\underset{\sim}{A} = \underset{\sim}{A}(t) = \underset{\sim}{E}^{(o)}(t) - \underset{\sim}{E}'(t) \tag{1.23}$$

and

$$\underset{\sim}{C}' = \underset{\sim}{C}'(t)$$

$\underset{\sim}{E}'$ and $\underset{\sim}{C}'$ being related by (2.14).

Now, Equation (1.14) contains $\underset{\sim}{\Omega}'(t)$, the (unknown) rotation tensor for the particle, and we can also derive equations for this tensor from Jeffrey's results. In fact, one can show easily that Jeffery's formula for rotation in the absence of torque can be expressed in the present notation as

$$\Delta\underset{\sim}{\Omega} + \underset{\sim}{C}'\cdot(\Delta\underset{\sim}{\Omega}) + (\Delta\underset{\sim}{\Omega})\cdot\underset{\sim}{C}' = \underset{\sim}{E}^{(o)}\cdot\underset{\sim}{C}' - \underset{\sim}{C}'\cdot\underset{\sim}{E}^{(o)} \tag{1.24}$$

where

$$\underset{\sim}{\Delta\Omega} = \underset{\sim}{\Omega}' - \underset{\sim}{\Omega}^{(o)} \tag{1.25}$$

$\underset{\sim}{\Omega}^{(o)}$ denoting the rotation tensor of the undistrubed flow. (Giesekus (1962) has put this result in a different form, involving a third-order tensor). Again, it follows from the preceding section, Equation (1.9), that for deforming ellipsoids the tensor $\underset{\sim}{E}^{(o)}$ in (1.24) should be replaced by the tensor $\underset{\sim}{A}$ of (1.23). Hence, with the approximation of small strain, the resulting equation for $\underset{\sim}{\Delta\Omega}$ yields, on solution by "successive approximations,"

$$\underset{\sim}{\Delta\Omega} = \underset{\sim}{A} \cdot \underset{\sim}{C}' - \underset{\sim}{C}' \cdot \underset{\sim}{A} + \mathcal{O}(C'^2) \tag{1.26}$$

where $\mathcal{O}(C'^2)$ denotes terms involving the squares of the components of $\underset{\sim}{C}'$.

It should also be pointed out here that, as is the case for a rigid ellipsoid, the resultant force on a deforming ellipsoid can readily be shown to vanish, which means in the present context that the ellipsoid moves with the mean velocity of the undisturbed flow, as presupposed by (1.3).

In summary now, we note that Equations (1.14), (1.22) and (1.26), together with the appropriate rheological equation for the particle relating $\underset{\sim}{E}'(t)$ to $\underset{\sim}{P}'(t)$ or, more generally, to the stress history $(\underset{\sim}{P}'(t_1), -\infty \leq t_1 \leq t)$ would represent four equations involving four unknown tensor quantities $\underset{\sim}{P}'$, $\underset{\sim}{C}'$, $\underset{\sim}{E}'$, and $\underset{\sim}{\Omega}'$. It appears that for a given velocity gradient tensor $\underset{\sim}{\Gamma}^{(o)}(t)$ this system should be determinate, subject of course to the appropriate set of initial conditions.

In closing here, we should emphasize that the above analysis is necessarily restricted to particles whose rheology is consistent with the assumption that the homogeneous surface stress of (1.22) implies finite homogeneous deformation. (Thus, in general, the analysis would not be applicable to droplets of a Newtonian fluid with a viscosity different from that of the surrounding fluid.) We shall consider below a specific rheological model for the particles, after some consideration of the macroscopic rheology of particle suspensions.

2. DILUTE SUSPENSIONS OF VISCOELASTIC SPHERES

Having at our disposal now the equations which govern the motion of individual, isolated viscoelastic spheres in Newtonian shear fields, we should like next to use them to determine rheological behavior of suspensions of such particles. However, despite the wealth of papers dealing with the rheology of dilute systems, it appears that none of the techniques previously employed are of sufficient generality to permit one to proceed systematically from a detailed knowledge of individual particle behavior, or "microrheology," to a prediction of the macroscopic behavior, or "macrorheology," of suspensions. Therefore, it is appropriate here to establish briefly the technique to be employed in the present work. This technique is essentially an extension of that already used by Giesekus (1962).

scopic scale, we have that

$$\iiint_{\mathcal{R}(t)} \underset{\sim}{\Gamma}(\underset{\sim}{r},t)dV = \frac{1}{2}\iiint_{\mathcal{V}'(t)} \{\underset{\sim}{\nabla}\underset{\sim}{v}(\underset{\sim}{r},t) + [\underset{\sim}{\nabla}\underset{\sim}{v}(\underset{\sim}{r},t)]^{\dagger}\}dV$$

$$= \frac{1}{2}\iint_{\mathcal{S}(t)} \{\underset{\sim}{v}(\underset{\sim}{r},t)\underset{\sim}{n} + \underset{\sim}{n}\,\underset{\sim}{v}(\underset{\sim}{r},t)\}dS = V\underset{\sim}{\Gamma}^{(o)}(t) \qquad (2.2)$$

where $\underset{\sim}{n}$ is the unit outer normal to $\mathcal{S}(t)$. The first equality here follows from the definition of $\underset{\sim}{\Gamma}$ and the second from an elementary result of vector calculus, provided that $\underset{\sim}{v}$ is continuous across the particle boundaries $\mathcal{S}'(t)$; finally, the third equality is a consequence of (3.1), together with the (dyadic) relation

$$\iint_{\mathcal{S}(t)} \underset{\sim}{r}\,\underset{\sim}{n}\,dS = V\,\underset{\sim}{I}$$

and its transpose, where V is the volume of $\mathcal{R}(t)$. Thus, by (2.2), $\underset{\sim}{\Gamma}^{(o)}(t)$ is seen to be identical to the <u>volume average</u> of the (microscopic) velocity-gradient tensor $\underset{\sim}{\Gamma}(\underset{\sim}{r},t)$.

We shall now assume that the sample, which is initially homogeneous, remains homogeneous under the above deformation and shall postulate that ensemble or "sample" averages of stress and velocity gradient can be replaced by their respective volume averages over the representative sample. Denoting these averages by the brackets < > we shall have then, by (2.2), that

$$< \underset{\sim}{\Gamma} > = \underset{\sim}{\Gamma}^{(o)} \qquad (2.3)$$

Letting, as before, $\underset{\sim}{P}(\underset{\sim}{r},t)$ denote the deviatoric stress tensor and noting that (1.21) holds everywhere in the fluid, we see readily then that

$$< \underset{\sim}{P} - 2 \mu \underset{\sim}{E} > \; = \; \varphi < \underset{\sim}{P}' - 2 \mu \underset{\sim}{E}' > \qquad (2.4)$$

where φ denotes the ratio of the volume of $\mathcal{R}'(t)$ to that of $\mathcal{R}(t)$, i.e., the <u>volume fraction</u> of the particulate phase $\mathcal{R}'(t)$, and where the primes denote an average over $\mathcal{R}'(t)$.

In light of (2.3), the relation (2.4) can be expressed as

$$< \underset{\sim}{P} > \; = \; 2 \mu \underset{\sim}{E}^{(o)} + \varphi < \underset{\sim}{P}' - 2 \mu \underset{\sim}{E}' > \qquad (2.5)$$

where $\underset{\sim}{E}^{(o)}$ is the deformation-rate tensor corresponding to the imposed deformation. It is a relatively easy matter to show that for rigid particles ($\underset{\sim}{E}' \equiv \underset{\sim}{0}$) the relation (2.5) reduces to that employed by Giesekus (1962).

In order now to apply (2.5) to the present problem, we shall assume, as is usual for dilute suspensions ($\varphi \ll 1$), that the interaction between particles is negligible and, following Happel and Brenner (1965), that the boundary condition of (2.1) can be replaced by that of (1.3). In other words, considering any arbitrarily chosen particle, the velocity distribution in its vicinity is assumed to be governed by (1.1), (1.3) and (1.5). Under these circumstances it is assumed then that Equations (1.22) to (1.26) will correctly describe the motion of any particle to terms of order φ^2, for given initial conditions on its orientation and deformation at some particular instant of time.

Since we have restricted this analysis to particles which are intrinsically spherical and have assumed the absence of torques on the particle, due to external fields or Brownian effects, it is reasonable to assume further that, subsequent to any initial state of rest or of isotropic stress in the sample of suspension, the motion and orientation of the individual particles should be identical, provided of course that the particles all have the same rheological behavior. Assuming this to be the case, we can then replace (2.5) simply by

$$< \underset{\sim}{P} > \; = \; 2\mu \, \underset{\sim}{E}^{(o)} + \varphi \, (\underset{\sim}{P}' - 2\mu \underset{\sim}{E}') \qquad (2.6)$$

where $\underset{\sim}{P}'(t)$ and $\underset{\sim}{E}'(t)$, the same now for <u>all</u> particles, are to be determined from the relations given in the preceding section, subject to the condition

$$\underset{\sim}{\Gamma}^{(o)} = \underset{\sim}{P}' = \underset{\sim}{E}' = \underset{\sim}{C}' = \underset{\sim}{0}$$

in some initial state, say, at $t = 0$.

As is usual now, the stress $<\underset{\sim}{P}>$ and the velocity-gradient $\underset{\sim}{\Gamma}^{(o)}$ are taken to represent quantities observed on the macroscopic level at a material "point" in the suspension.

2.2 Suspensions of viscoelastic spheres.

We consider now a suspension of viscoelastic spheres whose rheological behavior is assumed to be described by the constitutive equation

$$\underset{\sim}{C}'(t) = \mathcal{J}'\{\underset{\sim}{P}'(t)\} \qquad (2.7)$$

$\mathcal{J}'$ denoting a viscoelastic operator of the form

$$\mathcal{J}' = \frac{1}{2k} \cdot \frac{1 + a_1 \frac{\mathcal{D}'}{\mathcal{D}t} + a_2\left(\frac{\mathcal{D}'}{\mathcal{D}t}\right)^2 + \ldots}{1 + b_1 \frac{\mathcal{D}'}{\mathcal{D}t} + b_2\left(\frac{\mathcal{D}'}{\mathcal{D}t}\right)^2 + \ldots} \qquad (2.8)$$

where k, a_1, a_2,... and b_1, b_2,... are constants and where, for any second order tensors $\underset{\sim}{B}(t)$ associated with a particle, the operation $\mathcal{D}'/\mathcal{D}t$ is defined by

$$\frac{\mathcal{D}'}{\mathcal{D}t}\,\underset{\sim}{B}(t) = \frac{d}{dt}\,\underset{\sim}{B}(t) + \underset{\sim}{B}\cdot\underset{\sim}{\Omega}'-\underset{\sim}{\Omega}'\cdot\underset{\sim}{B} \qquad (2.9)$$

$\underset{\sim}{\Omega}'$ being the rotation tensor for the particle. Thus, for

$$a_1 = a_2 = \ldots = b_1 = b_2 = \ldots = 0 \qquad (2.10)$$

the particle is purely elastic and the constant k (with dimensions of stress) is the elastic modulus of the material.

The condition of small strain in the particle, which was postulated in Section 2, can now be formulated somewhat more precisely by requiring that the characteristic fluid stress on the particle be much smaller than the elastic modulus k. In terms of the macroscopic deformation tensor

$$< \underset{\sim}{E} > = \underset{\sim}{E}^{(o)}$$

this condition is essentially equivalent to the requirement that

$$\epsilon \overset{\text{def}}{=} \frac{\gamma\mu}{\cancel{2}k} \ll 1 \qquad (2.11)$$

where

$$\gamma = \sqrt{\cancel{}\tfrac{}{2}\,\underset{\sim}{E}^{(o)}:\underset{\sim}{E}^{(o)}} \qquad (2.12)$$

is the "shear rate" and μ is the viscosity of the suspending fluid.

It will be convenient in the following discussion to attribute formally an order of magnitude to various tensor quantities, and we shall employ for this purpose the O-notation already employed above, with the understanding that it applies to the individual components of tensors. In addition to the dimensionless number ϵ defined by (2.11) we shall henceforth include other physical parameters in the O-notation to indicate the physical dimensions involved.

By employing (1.14) and (1.26) and assuming henceforth that $\underset{\sim}{C}'$ is $O(\epsilon)$ we have then that

$$\underset{\sim}{E}' = \frac{\mathcal{D}\underset{\sim}{C}'}{\mathcal{D}t} - \underset{\sim}{E}'\cdot\underset{\sim}{C}'-\underset{\sim}{C}'\cdot\underset{\sim}{E}' \tag{2.13}$$
$$- \underset{\sim}{A}\cdot\underset{\sim}{C}'\cdot\underset{\sim}{C}'+2\underset{\sim}{C}'\cdot\underset{\sim}{A}\cdot\underset{\sim}{C}'-\underset{\sim}{C}'\cdot\underset{\sim}{C}'\cdot\underset{\sim}{A}+ O(\gamma\epsilon^3)$$

where the operator $\mathcal{D}/\mathcal{D}t$ is defined, for second order tensors $\underset{\sim}{B}(t)$ by

$$\frac{\mathcal{D}}{\mathcal{D}t}\underset{\sim}{B} = \frac{d\underset{\sim}{B}}{dt} - \underset{\sim}{\Omega}^{(o)}\cdot\underset{\sim}{B}+\underset{\sim}{B}\cdot\underset{\sim}{\Omega}^{(o)} \tag{2.14}$$

and the tensor $\underset{\sim}{A}$ is defined by (1.23).

We shall postulate further now that all terms of the second order in various kinematic tensors which describe the motion of the particle, $\underset{\sim}{C}'$, $\underset{\sim}{E}'$, $\mathcal{D}\underset{\sim}{C}'/\mathcal{D}t$, etc., can be neglected. In view of the time-derivatives involved in various of these tensors, it is necessary then that we place restrictions on the magnitudes of the time rates of change of certain quantities. However, being unable <u>a priori</u> to formulate such restrictions in a precise way, we shall assume for present purposes that the term $\mathcal{D}\underset{\sim}{C}'/\mathcal{D}t$ in (2.13) is $O(\epsilon\gamma)$, and, as a consequence, that $\underset{\sim}{E}'$ is formally $O(\epsilon\gamma)$. Hence (2.13) can in a formally consistent way be replaced by

$$\underset{\sim}{E}' = \frac{\mathcal{D}\underset{\sim}{C}'}{\mathcal{D}t} + O(\gamma\epsilon^2) \tag{2.15}$$

Furthermore, we can then simplify (1.22) to

$$\underset{\sim}{P}' = 5\mu\{\underset{\sim}{E}^{(o)}-\underset{\sim}{E}' + \frac{3}{7}(\underset{\sim}{E}^{(o)}\cdot\underset{\sim}{C}'+\underset{\sim}{C}'\cdot\underset{\sim}{E}^{(o)}) - \frac{2}{7}(\underset{\sim}{E}^{(o)}:\underset{\sim}{C}')\underset{\sim}{I}\} \tag{2.16}$$
$$+ 2\mu\underset{\sim}{E}' + O(\mu\gamma\epsilon^2)$$

and, with appropriate restrictions on higher-order time derivatives, the expression (2.8) for the operator $\mathcal{J}'$ can be replaced in the following analysis by

$$\mathcal{J} = \frac{1}{2k}\,\frac{1 + a_1\left(\frac{\delta}{\delta t}\right) + a_2\left(\frac{\delta}{\delta t}\right)^2 + \dots}{1 + b_1\left(\frac{\delta}{\delta t}\right) + b_2\left(\frac{\delta}{\delta t}\right)^2 + \dots} \tag{2.17}$$

obtained by substituting $\delta/\delta t$ for $\delta'/\delta t$.

Hence, by (2.7), (2.16) and (2.17) we find that

$$\mathcal{J}\{\underset{\sim}{P}'\} = \underset{\sim}{C}' = 5\mu\,\mathcal{J}\{\underset{\sim}{E}^{(o)} - \underset{\sim}{E}'$$

$$+ \frac{3}{7}(\underset{\sim}{E}^{(o)}\cdot\underset{\sim}{C}' + \underset{\sim}{C}'\cdot\underset{\sim}{E}^{(o)}) - \frac{2}{7}(\underset{\sim}{E}^{(o)}:\underset{\sim}{C}')\underset{\sim}{I}\} + 2\mu\,\mathcal{J}\{\underset{\sim}{E}'\} + O(\epsilon^3)$$

or formally that

$$\underset{\sim}{C}' = 5\mu\,\mathcal{J}\{\underset{\sim}{E}^{(o)}\} + O(\epsilon^2) \tag{2.18}$$

Substitution of (2.18) into (2.16) gives then

$$\underset{\sim}{P}' = 5\mu\,\underset{\sim}{E}^{(o)} - 3\mu\underset{\sim}{E}' + \frac{25\mu^2}{7}\,[3(\underset{\sim}{E}^{(o)}\cdot\mathcal{J}\{\underset{\sim}{E}^{(o)}\}$$

$$+ \mathcal{J}\{\underset{\sim}{E}^{(o)}\}\cdot\underset{\sim}{E}^{(o)}) - 2(\underset{\sim}{E}^{(o)}:\mathcal{J}\{\underset{\sim}{E}^{(o)}\})\underset{\sim}{I}] + O(\mu\gamma\epsilon^2) \tag{2.19}$$

Employing these approximations and writing henceforth $\underset{\sim}{E}$ for $\underset{\sim}{E}^{(o)} \equiv \langle \underset{\sim}{E} \rangle$ and $\underset{\sim}{P}$ for $\langle \underset{\sim}{P} \rangle$ we find then, on substitution of (2.19) into (2.6), that

$$\underset{\sim}{P} = 2\mu(1 + \frac{5}{2}\varphi)\underset{\sim}{E} + \frac{25}{7}\mu^2\varphi\,[3(\underset{\sim}{E}\cdot\mathcal{J}\{\underset{\sim}{E}\} + \mathcal{J}\{\underset{\sim}{E}\}\cdot\underset{\sim}{E})$$

$$-2(\underset{\sim}{E}:\mathcal{J}\{\underset{\sim}{E}\})\underset{\sim}{I}] - 5\mu\varphi\underset{\sim}{E}' \tag{2.20}$$

In order now to eliminate $\underset{\sim}{E}'$ from this equation we define an operation $\mathcal{M}$ by

$$\mathcal{M}\{\underset{\sim}{B}\} = \frac{\delta}{\delta t}\,\mathcal{J}\{\underset{\sim}{B}\} = \mathcal{J}\{\frac{\delta \underset{\sim}{B}}{\delta t}\}$$

where $\mathcal{J}$ is defined now by (2.17). Next, applying this operation to (2.6) and taking account of (2.7) and (2.15) and (2.17), we find that

$$\mathcal{M}\{\underset{\sim}{P}\} = 2\mu\,\mathcal{M}\{\underset{\sim}{E}\} + \varphi\,[\underset{\sim}{E}'-2\mu\mathcal{M}\{\underset{\sim}{E}'\}] + O(\varphi\gamma\epsilon^2) \tag{2.21}$$

Finally, by applying the operator

$$1 - 2\mu\,\mathcal{M}$$

to both sides of (2.20) and subtracting the resulting equation from (2.21), we have, as the rheological constitutive equation for the suspension,

$$\underset{\sim}{P} + 3\mu\mathcal{J}\{\frac{\delta\underset{\sim}{P}}{\delta t}\} = 2\mu\,[(1+\frac{5}{2}\varphi)\underset{\sim}{E} + 3\mu\,(1-\frac{5}{3}\varphi)\mathcal{J}\{\frac{\delta\underset{\sim}{E}}{\delta t}\}] + \frac{25}{7}\varphi\mu^2\,[3(\underset{\sim}{E}\cdot\mathcal{J}\{\underset{\sim}{E}\}+\mathcal{J}\{\underset{\sim}{E}\}\cdot\underset{\sim}{E})-2(\underset{\sim}{E}:\mathcal{J}\{\underset{\sim}{E}\})\underset{\sim}{I}] \tag{2.22}$$

to terms which are formally $O(\gamma\mu\varphi\epsilon^2)$. It will be recalled that the operator $\mathcal{J}$ is defined by (2.17) and the derivative $\delta/\delta t$ by (2.14) while φ is the volume fraction of the particulate phase.

In order for (2.22) to apply to an arbitrary flow field of the suspension in question it is necessary to interpret $\underset{\sim}{P}$ and $\underset{\sim}{E}$ as the local spatial values of the macroscopic stress and deformation-rate tensors $\underset{\sim}{P}(\underset{\sim}{x},t)$ and $\underset{\sim}{E}(\underset{\sim}{x},t)$, say, and to postulate that the suspended particles are sufficiently small that higher-order derivatives of the macroscopic velocity field do not affect the rheological behavior of the suspension, i.e., that the assumption of homogeneous strain, for the macroscopic sample volume considered above, remains valid. Moreover, since the particles move with the mean velocity of the fluid, the derivative $\delta/\delta t$ of (2.14) can be interpreted as the Jaumann derivative, which for a second-order tensor field $\underset{\sim}{B}(\underset{\sim}{r},t)$ is defined by

$$\frac{\mathcal{D}\underset{\sim}{B}}{\mathcal{D}t} = \frac{D}{Dt}\underset{\sim}{B} + \underset{\sim}{B}\cdot\underset{\sim}{\Omega} - \underset{\sim}{\Omega}\cdot\underset{\sim}{B} \tag{2.23}$$

where $\underset{\sim}{\Omega} = \underset{\sim}{\Omega}(\underset{\sim}{r},t)$ is the local rotation tensor and where

$$\frac{D}{Dt}\underset{\sim}{B} = \frac{\partial\underset{\sim}{B}}{\partial t} + \underset{\sim}{v}\cdot\underset{\sim}{\nabla}\underset{\sim}{B} \tag{2.24}$$

is the material derivative, with $\underset{\sim}{v} = \underset{\sim}{v}(\underset{\sim}{r},t)$ denoting the local flow velocity.

Considering now the simplest example, that of purely elastic spheres where (2.10) holds in (2.17), we see that (2.22) reduces to

$$\begin{aligned}\underset{\sim}{P} + \tau\frac{\mathcal{D}\underset{\sim}{P}}{\mathcal{D}t} &= 2\mu\left[(1 + \tfrac{5}{2}\varphi)\underset{\sim}{E} + \tau(1 - \tfrac{5}{3}\varphi)\frac{\mathcal{D}\underset{\sim}{E}}{\mathcal{D}t}\right] \\ &+ \frac{50}{7}\varphi\mu\tau\left[\underset{\sim}{E}\cdot\underset{\sim}{E} - \tfrac{1}{3}(\underset{\sim}{E}:\underset{\sim}{E})\underset{\sim}{I}\right]\end{aligned} \tag{2.25}$$

where

$$\tau = \frac{3\mu}{2k} \tag{2.26}$$

is a characteristic time parameter for the system.

As one can readily verify, the equation obtained by dropping the second term on the right-hand side (with coefficient $\varphi\mu\tau$) from (2.25) is equivalent, to terms of $\mathcal{O}(\varphi^2)$, to the equation derived by Fröhlich and Sack (1946) for the special case of irrotational flow, $\underset{\sim}{\Omega} \equiv 0$. Our analysis shows, first of all, that the appropriate generalization of Fröhlick and Sack's equation to rotational flows consists of replacing their time derivative by the Jaumann derivative, thus answering a question which has been raised by Oldroyd (1953).

In addition, the result derived here contains nonlinear terms in the deformation-rate tensor $\underset{\sim}{E}$ which, according to the present analysis, arise from the ellipticity of the deformed spheres. Therefore it would appear that Fröhlich and Sack's approximation of replacing the particle by a sphere, in order to simplify boundary conditions, is in error. Of course, the terms in question are multiplied by $\tau\varphi$ and it might be argued that these terms should be discarded since we have already neglected terms of order φ^2 as well as those of order $\epsilon^2 = (\tau\gamma)^2$. However, by adopting this point of view, we would be forced to replace terms like $\tau(1 - \frac{5}{3}\varphi)$, the coefficient of $\mathcal{D}\underset{\sim}{E}/\mathcal{D}t$ in (2.25), by τ alone, in our result as well as in that of Fröhlich and Sack. This is obviously undesirable, for by such reasoning one could eliminate elastic effects entirely from (2.25) reducing it to the Einstein equation

$$\underset{\sim}{P} = 2\mu\left(1 + \frac{5}{2}\varphi\right)\underset{\sim}{E}$$

for rigid spheres.

In closing here, it is interesting to note that (2.25) is a special case of a general rheological equation already proposed by Oldroyd (1958). By means of the analysis presented in his paper one deduces that, in a steady simple-shear flow, a fluid described by (2.25) would exhibit "shear thinning" and unequal normal stresses in all three directions, all directly proportional to τ, while for flow between rotating cylinders the fluid should exhibit a positive Weissenberg climbing effect.

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